



# Activated carbon supported cobalt catalysts for advanced oxidation of organic contaminants in aqueous solution

Pradeep R. Shukla, Shaobin Wang\*, Hongqi Sun, H. Ming Ang, Moses Tadé

Department of Chemical Engineering and CRC for Contamination Assessment and Remediation of the Environment (CRC CARE), Curtin University of Technology, GPO Box U1985, Perth, WA 6845, Australia

## ARTICLE INFO

### Article history:

Received 6 April 2010

Received in revised form 25 August 2010

Accepted 4 September 2010

Available online 15 September 2010

### Keywords:

Activated carbon

Cobalt

Phenol

Advanced oxidation process

Water treatment

## ABSTRACT

A heterogeneous cobalt catalyst was prepared by impregnation of cobalt ion on an activated carbon (AC) and used to activate peroxymonosulphate (PMS) for advanced oxidation of phenol in aqueous solution. The Co/AC catalyst was characterised by several techniques such as XRD, EDS, SEM, and TGA. It was found that  $\text{Co}_2\text{O}_3$  was the major form of Co species and was homogeneously distributed on the activated carbon surface. Co/AC exhibited high activity in oxidation of phenol with sulphate radicals and 100% decomposition and 80% TOC removal could be achieved in 60 min at the conditions of 500 ml phenol solution of 25 ppm, 0.1 g catalyst and 1 g peroxymonosulphate. The catalyst also exhibited stable performance after several rounds of regeneration. Several operational parameters such as catalyst and oxidant amount, temperature on the rate of oxidation were found to influence the phenol oxidation.

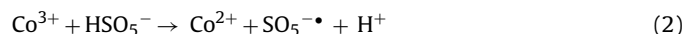
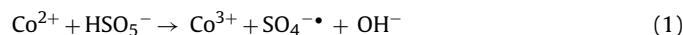
© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

Discharging of water pollutants like phenol, chlorophenols, BTEX, etc., even in small concentrations poses a great threat to the environment. Various chemical techniques such as thermal destruction, wet air oxidation, catalytic oxidation (both homogeneous and heterogeneous oxidation), ozonation, etc., have been researched and employed to oxidise the pollutants to harmless end products,  $\text{CO}_2$  and water [1–5]. Among the available oxidation techniques, heterogeneous catalytic oxidation is generally carried out at normal temperature and pressure. Thus it gives added advantage of energy efficiency. Use of economically available catalysts for pollutant oxidation, which can also be regenerated, will certainly over-shadow other techniques. Finally the problem of harmful intermediates can be easily countered by a well designed system to assure complete oxidation of the pollutants.

Among various techniques of catalytic oxidation for water and wastewater treatment, Fenton reaction involving hydrogen peroxide and Fe ion has been extremely popular. This reaction follows a specific oxidation pathway, generally initiated due to the formation of free hydroxyl radicals in the presence of  $\text{Fe}^{2+}$  ions. These hydroxyl radicals are extremely reactive and readily oxidise organic pollutants into harmless end products. The oxidation by the Fen-

ton reagent or Fenton like reagent has been used successfully for decades [6]. To enhance the performance of the process, various modifications have been proposed such as employing UV irradiation [7–9] and ultrasonic radiation [10]. Similar to the activity of hydrogen peroxide for the degradation of organic pollutants, alternative oxidants such as peroxymonosulphate and persulphate have been found to be highly effective in chemically mineralising various organic contaminants. Recent research carried out by some investigators [11–14] has successfully proven the applicability of cobalt ion as an efficient catalyst for the activation of peroxymonosulphate to produce sulphate radicals for oxidation of organic compounds. The activation reaction proceeds as follows [12].



The oxidation rate of organics using sulphate radicals was reported to be reasonably appreciable as compared to the conventional Fenton reagent and is also less dependent on the reaction pH, thus providing a suitable alternative to the convenient Fenton reagent for pollutant oxidation [12]. Nonetheless, the major problem confronting the use of the technique is the toxicity associated with cobalt ions, leading to several health problems such as asthma, pneumonia and other lung problems. In order to restrict the discharge of cobalt in water, a heterogeneous cobalt catalyst is highly demanded. For sulphate radical systems, few heterogeneous  $\text{Co}^{2+}$  based catalysts have been investigated including  $\text{Co}_3\text{O}_4$  [11,15,16] and oxide supported Co catalysts [17,18]. The heterogeneous

\* Corresponding author. Tel.: +61 8 9266 3776; fax: +61 8 9266 2681.  
E-mail address: [shaobin.wang@curtin.edu.au](mailto:shaobin.wang@curtin.edu.au) (S. Wang).

Co<sub>3</sub>O<sub>4</sub> exhibited strong leaching of Co<sup>2+</sup>. Yang et al. [17,18] also found Al<sub>2</sub>O<sub>3</sub>-, TiO<sub>2</sub>- and SiO<sub>2</sub>-supported Co catalysts exhibited Co<sup>2+</sup> leaching depending on the metal–support interaction. Zhang et al. [19] recently investigated various oxide supported Co catalysts for dye degradation and found that Co/MgO showed less Co<sup>2+</sup> leaching and stable performance. We also investigated several Co exchanged zeolites for phenol degradation and found that Co-ZSM5 exhibited stable performance with much lower Co leaching [20].

It is well known that activated carbon is a good adsorbent and catalyst support for both gas and aqueous phases. Combination of adsorptive property of activated carbon and supported active component as a catalyst will provide a good route for aqueous phase reaction. In this paper, we report a Co-based activated carbon catalyst for advanced oxidation of phenol using peroxymonosulphate, which exhibits fast and high activity with stable performance after several runs of testings.

## 2. Experimental

### 2.1. Synthesis of cobalt impregnated activated carbon

An activated carbon (AC) sample was obtained from BDH Chemicals and was crushed into powder. Then it was washed with ultra-pure water and dried in an oven. The Co loaded activated carbon was prepared by a wet impregnation technique. A fixed amount of AC was added to a cobalt nitrate solution and the suspension was stirred for 24 h and evaporated in a rotary evaporator at 50 °C under vacuum. After that the solid was calcined at 750 °C for 6 h under Ar flow and was further calcined at 350 °C under air to oxidise the reduced cobalt ion and metal. It has been reported that metal oxide can be reduced to metal species by carbon support under inert gas atmosphere at high temperature [21]. Thus, the calcination of Co/AC in air would re-oxidise Co metal to oxides. The calcined Co/AC sample was washed several times with milli-Q water to remove the loosely bonded cobalt and then was stored in a desiccator until use.

### 2.2. Characterisation of catalyst

The texture, morphology and semi quantitative analyses of Co/AC sample were done using SEM with both secondary and backscatter electrons. Carbon was simply sprinkled on the stub and was analysed. The elemental composition was determined using the energy dispersive X-ray spectroscopy (EDS). The EDS analysis was carried out at several points in the region and averaged to obtain the representative results. The structural features and the mineralogy of the samples were studied from X-ray diffraction patterns obtained on a Siemens XRD instrument, using filtered Cu K $\alpha$  radiation with accelerating voltage of 40 kV and the current of 30 mA. The sample was scanned at 2 $\theta$  from 5 to 70°. Finally, the relative amount of cobalt oxide on Co/AC catalysts was determined by burning the carbon under air and measuring the weight loss using a TG analyser.

### 2.3. Kinetic study of phenol oxidation

The catalytic oxidation of phenol was carried out in a 500 ml reactor containing 25 ppm of phenol solution, unless otherwise stated. The reactor was attached to a stand and dipped in a water bath with a temperature controller. The reaction mixture was stirred constantly to maintain homogeneous solution. A known amount of oxidant, oxone (peroxymonosulphate, DuPont's triple salt, 2KHSO<sub>5</sub>·KHSO<sub>4</sub>·K<sub>2</sub>SO<sub>4</sub>) obtained from Aldrich, was added to the mixture and allowed to dissolve before the reaction. Later a fixed quantity of Co/AC catalyst depending on the predefined reac-

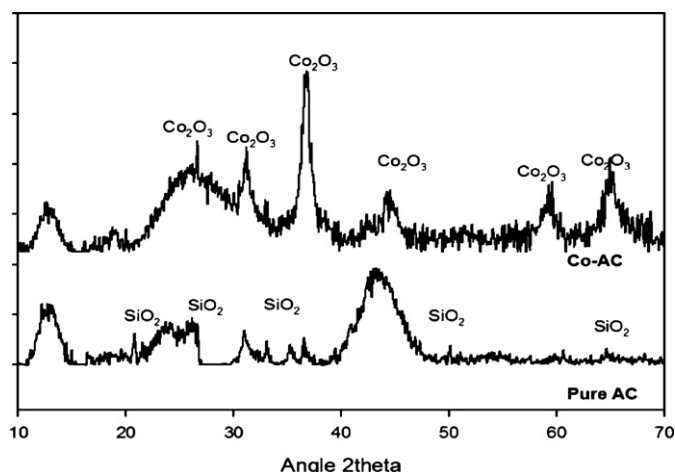


Fig. 1. XRD spectra of AC and Co/AC.

tion parameter was added to start the reaction. The reaction was carried on for 2 h. At a fixed interval, 0.5 ml sample was withdrawn using a syringe filter into a HPLC vial, and was added 0.5 ml of methanol to quench the reaction. The concentration was analysed using a HPLC with a UV detector at the wavelength of 270 nm. The column used was C-18 and the mobile phase was 30% CH<sub>3</sub>CN and 70% water. For a comparison, a homogeneous oxidation with cobalt ions and oxone was also conducted by addition of the chemicals into the phenol solution simultaneously. The Co<sup>2+</sup> concentration was kept as the same as the Co loaded on AC.

For selected samples, total organic content (TOC) was determined using a Shimadzu TOC-5000 CE analyser. For the measurement of TOC, 5 ml sample was extracted at a fixed interval and quenched with 5 ml of 3 M sodium nitrile solution and then analysed on the TOC analyser. The concentration of peroxymonosulphate was determined by titration against sodium thiosulphate. In each test, 5 ml of reaction mixture containing peroxymonosulphate was mixed with 2 g KI and was shaken vigorously. Then 0.2 g of Vitrx indicator was added and left for 15 min. Finally, 1 ml of glacial acetic acid was added to the solution and shaken well. The resultant mixture was titrated with sodium thiosulphate.

## 3. Results and discussion

### 3.1. Characterisation of cobalt impregnated activated carbon catalyst

The XRD spectra of carbon support and Co/AC catalyst are shown in Fig. 1. The carbon support presented as amorphous phase with minor peaks at 20.8, 26.6, 36.5, 50.1 and 68.1°, which are attributed to the presence of mineral SiO<sub>2</sub>. The presence of trace quantity of silica was also identified by the EDS analysis as discussed later in the section. The spectra of Co/AC catalyst showed distinct peaks of cobalt oxide crystallites (Co<sub>3</sub>O<sub>4</sub>) at 26.5, 31.5, 37.2, 59.5 and 65.7°. In addition, a few mini peaks obtained in the region between 40 and 50° were generally diffracted from the crystalline carbon samples after high temperature treatment.

The morphology of Co/AC and cobalt distribution in the catalyst sample was observed from the analysis of SEM images (Fig. 2). Fig. 2a shows the SEM image obtained using the secondary electron detector (SE). It was found that the milled sample had a diverse shape and size in the range of 5–150 micrometer. The same region observed using a backscattered detector (BSE) in Fig. 2b showed the presence of specks of cobalt oxides as the brighter region in the large particles. It was observed that the cobalt oxide particles were well assimilated in the carbon samples.

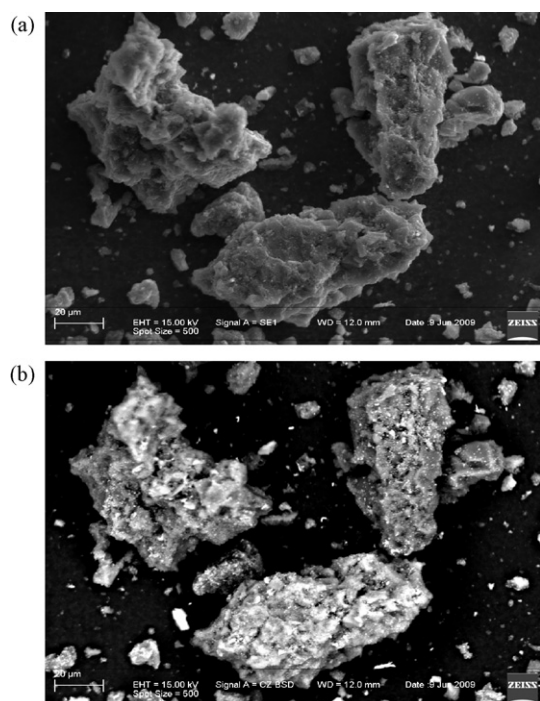


Fig. 2. SEM images of Co/AC. (a) SE detector and (b) BSE detector.

Additionally, a few small individual bright particles observed around the carbon particles appeared to be an individual cobalt oxide particle (Fig. 2b). Nevertheless an elemental analysis using the EDS study on the particle suggested the presence of both cobalt and carbon elements, signifying that the finer carbon particles were completely coated by a layer of cobalt oxide. The homogeneous distribution of cobalt in the carbon sample was confirmed by several EDS analyses on a small region by varying the accelerating voltage (keV), thereby generating the electrons of varying energy which penetrated to different depths of the sample. The spectra obtained at the different keVs help in comparing the elemental composition at different layers in the carbon particle. Fig. 3 shows the EDS spectra obtained at different keVs. As seen the spectra showed the presence of cobalt, silicon, oxygen and carbon. For all the spectra, the intensity of these peaks was increased with the increasing keV. The characteristic  $K\alpha$  and  $K\beta$  peaks of cobalt are obtained at 6.93 and 7.65 keV, respectively. At 15 keV, Co peak was much stronger, suggesting that Co ion was diffused into the inner pores of AC during the impregnation.

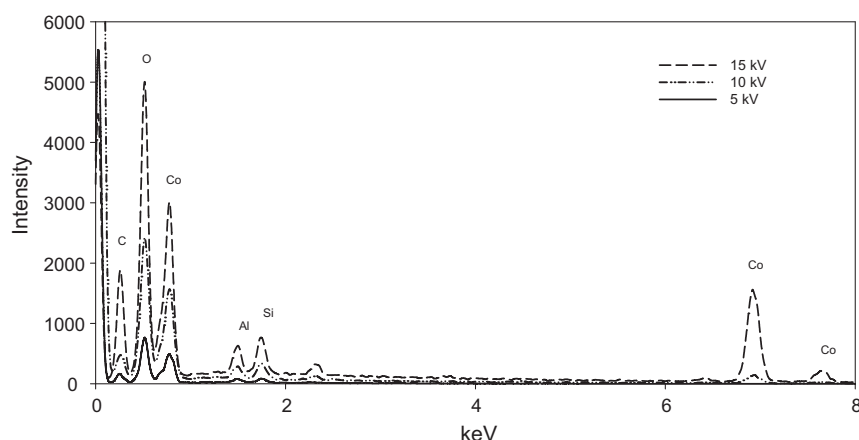


Fig. 3. EDS spectra of Co/AC catalyst particle at different accelerating voltages.

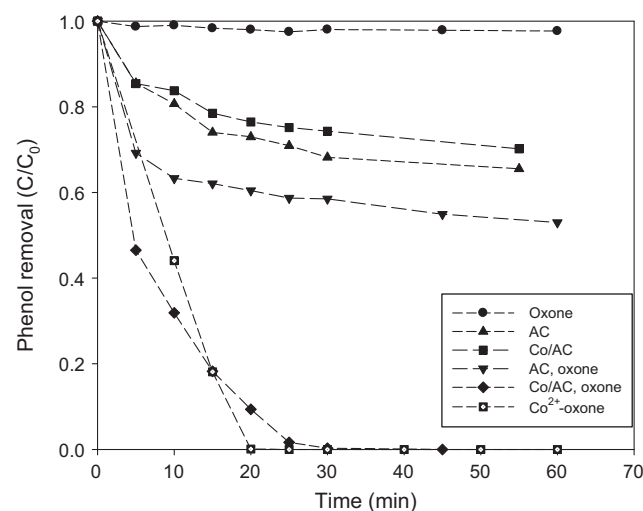


Fig. 4. Preliminary test of catalytic oxidation of phenol using AC and Co/AC [ $C_{ph}$ : 25 ppm, 0.2 g/l catalyst, 25 °C].

### 3.2. Preliminary study of phenol oxidation using catalysts

Fig. 4 displays the normalised phenol concentration profiles under various experimental conditions for adsorption and reaction. It is seen that AC and Co/AC showed phenol adsorption and AC presented a higher adsorption than the Co/AC. During 1 h period, phenol adsorption approached equilibrium on both materials. AC showed about 35% phenol removal and Co/AC produced about 30% phenol reduction in concentration. This difference in phenol adsorption on AC and Co/AC was due to the loading of  $Co_2O_3$  on AC surface, which reduced the surface area and pore volume. From the figure, it is also seen that phenol removal would not change significantly for the case of oxone without any solid, suggesting no reaction occurring if only oxone is in the solution. However, if AC was present in the solution with oxone, phenol concentration showed a gradual decrease and the reduction in phenol concentration was higher than that of AC adsorption. After 1 h, phenol removal was about 48%. This suggests that AC could possibly activate oxone to produce sulphate radicals, which reaction is shown in Eq. (3). However, due to low reactivity of persulphate radical ( $SO_5^{\cdot-}$ ), removal of phenol in AC/oxone was only about 10% higher than that in AC. For Co/AC with oxone, phenol removal rate was much fast and 100% removal could be achieved in 30 min. This rate is comparable to the homogeneous process and much better than Co-ZSM5 [20]. The activation of oxone by  $Co_2O_3$  could be presented

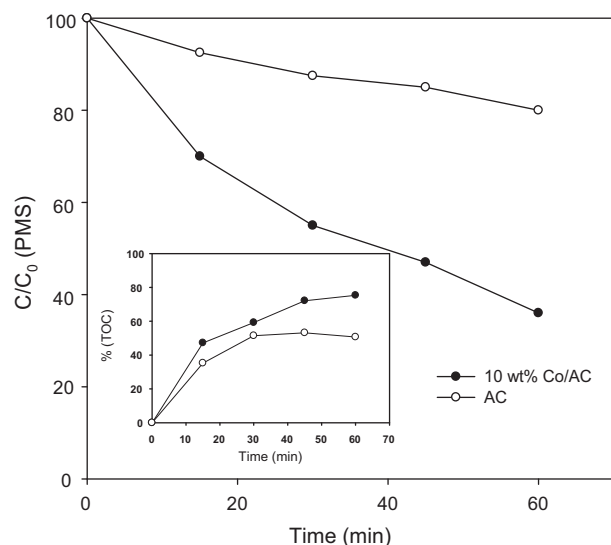
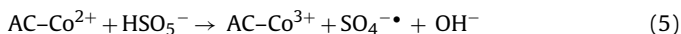
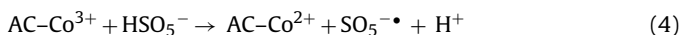


Fig. 5. Oxone consumption in the presence of AC and Co/AC [ $C_{ph}$ : 25 ppm, 0.2 g/l catalyst, 25 °C, 2 g/l oxone]. Insert figure showing the extent of TOC removal.

by Eqs. (4) and (5). Due to the production of  $SO_4^{\bullet-}$  and  $SO_5^{\bullet-}$  in a fast rate, phenol decomposition would achieve in a very short time.



Few investigations have been reported for heterogeneous Co-based catalysts for organic decomposition using sulphate radicals. Anipsitakis et al. [15] studied the heterogeneous activation of oxone in water using cobalt oxides,  $CoO$  and  $Co_3O_4$ , and found that only  $Co_3O_4$  activated oxone heterogeneously with significant cobalt leaching from these particles during the degradation process. Yang et al. [17,18] investigated  $Al_2O_3$ -,  $TiO_2$ - and  $SiO_2$ -supported Co catalysts for the degradation of 2,4-dichlorophenol in water and found that  $Co_3O_4$  was the only Co species present on the supported catalysts. The supported Co catalysts showed activity of  $Co/SiO_2 > Co/TiO_2 > Co/Al_2O_3$  and the extent of leaching problem was dependent on the cobalt-support interaction. Zhang et al. [19] reported a study of organic dye degradation on various supported Co catalysts via sulphate radical approach. They found that  $Co/MgO$  exhibited better activity than others due to higher dispersion of  $Co_3O_4$ . In this investigation, XRD analysis showed  $Co_2O_3$  as the only Co species on Co/AC catalyst, suggesting that  $Co_2O_3$  particles will be the active sites for activation of peroxymonosulphate.

The extent of phenol removal in the presence of both AC and Co-AC was correlated with the amount of TOC removal from the solution as seen from Fig. 5 (insert). The test in AC-PMS system showed almost 45% removal of TOC, which is similar to the extent of phenol adsorption on the solid. During the same test, almost 49% loss of oxidant was measured (Fig. 5). In the case of combined adsorption and reaction in the presence of Co-AC/PMS system, almost 80% TOC was removed from the solution. The removal of TOC is in agreement with the catalytic reaction taking place, however, the TOC removal was less than the corresponding extent of phenol removal, implying the presence of reaction intermediates in the solution. As seen from the oxidant concentration profile (Fig. 5), the loss of PMS oxidant in AC/PMS system suggests the possible interaction of AC with oxone resulting in decomposition of the oxidant and generation of active sulphate radical ( $SO_5^{\bullet-}$ ). However, the activity of peroxymonosulphate radical for the oxidation of organic contaminants is minimal. In the case of Co/AC based system, around

70% oxidant was found to be consumed for the generation of active radicals and other reactions with intermediates resulting in higher phenol oxidation.

### 3.3. Effects of reaction parameters on phenol degradation

Fig. 6 illustrates phenol removal percentage at varying initial concentrations (25–100 ppm). The inserted figure shows the relationship between initial rate of reaction and initial phenol concentration. One can see that phenol degradation depended on initial concentration. At high phenol concentration, removal efficiency would be decreased. At the concentration less than 100 ppm, 100% removal could be achieved within 2 h, however, the removal efficiency for 100 ppm would be 80% at 2 h.

In order to estimate the kinetics, a general pseudo first order kinetics for phenol decay was assumed in the present system.

$$\frac{dC_{ph}}{dt} = -(k_{app}C_{ph}) \quad (6)$$

where  $k_{app}$  is the apparent first order rate constant of phenol degradation,  $C_{ph}$  is the concentration of phenol at any instant time,  $t$ . The apparent rate constant considered in the given case is the global rate constant comprising of several intermediate steps of adsorption, oxidation, and desorption. The concentration profile of phenol removal can thus be represented as follows.

$$C_{ph} = C_{ph0} \exp(-k_{app}t) \quad (7)$$

Data fitting showed that the phenol removal could be described by the first order kinetics. The initial rate constant was also obtained at varying phenol concentrations. The insert figure shows that the initial rate of phenol reaction increased with the increasing phenol concentration.

The effect of cobalt loading on AC on the rate of phenol oxidation is shown in Fig. 7. Higher amount of cobalt loading provides additional sites for generation of active sulphate radical thereby enhancing the rate of reaction. The increase in cobalt loading from 2.5 to 5 wt.% resulted in almost double of the rate constant, however, a further increase of Co loading on AC to 10 wt.% showed a comparatively smaller improvement in the extent of reaction. The increase in the cobalt loading would enhance the rate of activation of PMS to generate the active sulphate radical, resulting in an increase in the rate of phenol removal. However, the high amount of cobalt loading would reduce the extent of phenol adsorption, thus the extent of phenol removal is capped by the extent of PMS and phenol adsorbed onto the AC surface.

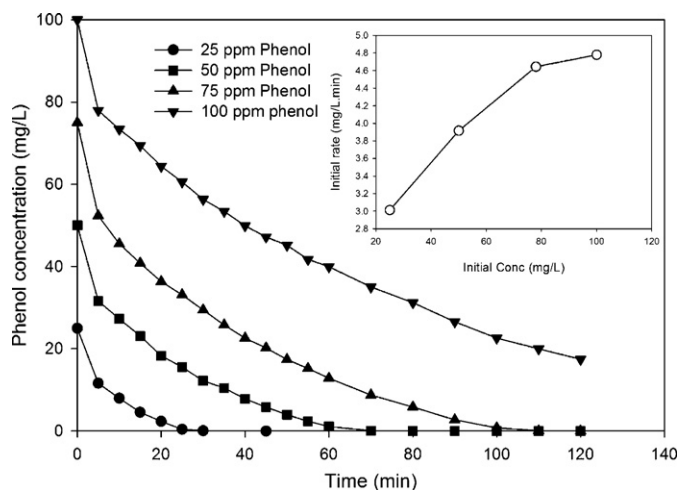


Fig. 6. Phenol degradation kinetics in the presence of Co/AC and oxone [2 g/l oxone, 0.2 g/l catalyst, 25 °C].



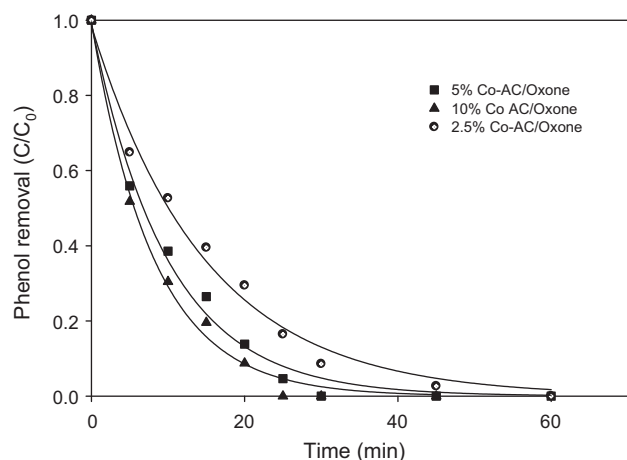


Fig. 7. Phenol degradation kinetics in the presence of Co/AC catalyst having different cobalt loadings [ $C_{ph}$ : 25 ppm, 2 g/l oxone, 0.2 g/l catalyst, 25 °C].

Fig. 8 displays the variation of normalised phenol concentration as a function of oxidant concentration in the solution. The rate of reaction was observed to improve with the increasing oxidant concentration. An enhancement of the initial rate was as much as 3 times for 1 g/L PMS when compared with 0.5 g/L of PMS.

Fig. 9 shows the effect of Co/AC loading in solution on phenol removal. Similar to the behaviour of PMS oxidant, an increase in Co/AC content in the solution increased the phenol removal efficiency. At 0.05 g/L, phenol removal would be 80% at 120 min, while it would be 100% at 30 min at Co/AC loading of 2 g/L. The incremental addition of the catalyst would increase adsorption site and also provide extra catalyst for activation of peroxymonosulphate, and thus would result in a significant enhancement of the rate of reaction.

The reaction temperature would also play a significant role in phenol oxidation reaction. Fig. 10 shows the effect of temperature on phenol removal on Co/AC. It was observed that the rate of reaction increased significantly with the rise in temperature with complete removal of phenol being observed within 5 min at 50 °C. Using the first order kinetic rate constant, the activation energy for this heterogeneous phenol decomposition was found to be 59.7 kJ/mol. It is noted that phenol removal in Co/AC–PMS system would be ascribed to adsorption and oxidation. In this investigation, it would be difficult to distinguish the contribution from each part, thus, the apparent activation energy would refer to the combined processes.

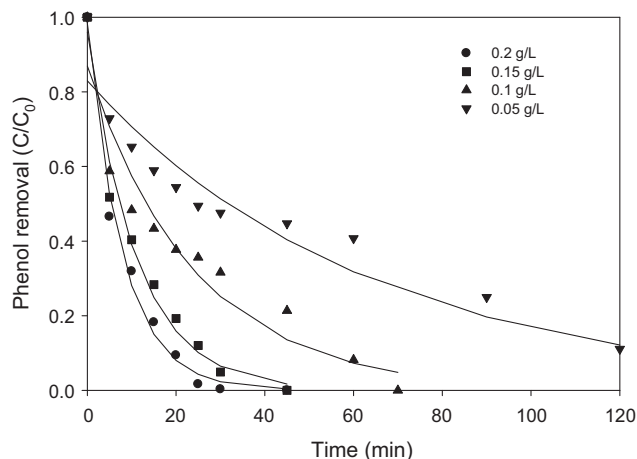


Fig. 8. Phenol degradation at different catalyst loadings [ $C_{ph}$ : 25 ppm, 2 g/l oxone, 25 °C].

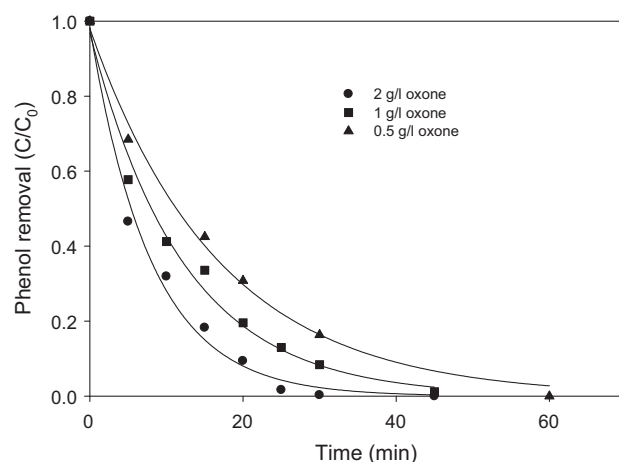


Fig. 9. Phenol degradation at different oxidant amounts [ $C_{ph}$ : 25 ppm, 0.2 g/l catalyst, 25 °C].

### 3.4. Leaching of cobalt and reusability of Co/AC catalyst

For the heterogeneous phenol oxidation by using Co/AC and PMS, it is essential to examine the catalytic efficiency of the spent catalyst. After each reaction, the catalyst was recovered from the reaction mixture by filtration through 0.5 micron filter and washed with distilled water several times to remove any organic component adsorbed on the surface. The acquired catalyst was reused for the oxidation of phenol and the results are shown in Fig. 11.

As seen from the figure, Co/AC catalyst activity showed somewhat deactivation but at much less extent in four runs of tests. The rate of phenol oxidation remained similar in the first and second performance while it decreased slightly in the third and fourth runs, suggesting that a small amount of cobalt was probably leached out from the carbon catalyst. Determination of Co ion in solution showed undetectable Co ion in the solution. However, the saturation of the carbon support with the contaminant may also account for the reduction in the reaction rate. Table 1 shows the rate constants and Co content of the fresh and regenerated Co/AC catalyst in each run. It is seen that the rate constants in the first and second runs were much closer and showed slight decrease in the third and fourth runs.

A thermogravimetric analysis was carried out to determine the relative amount of cobalt on AC. The weight loss of the first and

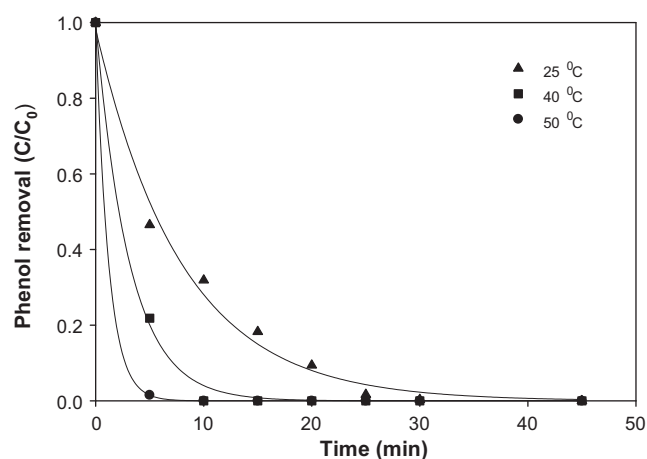
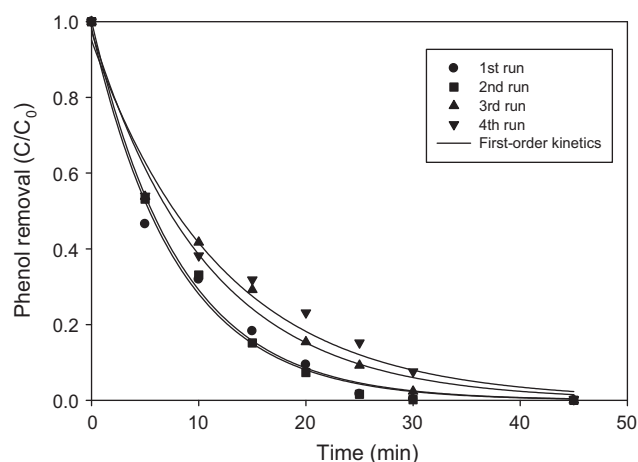


Fig. 10. Phenol degradation at different temperatures. [ $C_{ph}$ : 25 ppm, 0.2 g/l catalyst, 2 g/l oxone].



**Fig. 11.** Degradation of phenol in multiple use of Co-AC catalyst [ $C_{ph}$ : 25 ppm, 2 g/l oxone, 0.2 g/l catalyst, 25 °C].

**Table 1**  
Results of Co/AC tests in different runs.

Test no.	Rate constant ( $\text{min}^{-1}$ )	$R^2$	Co (wt.%)
Co/AC 1st use	0.125	0.991	11.8
Co/AC 2nd use	0.123	0.996	11.0
Co/AC 3rd use	0.0930	0.986	9.23
Co/AC 4th use	0.0827	0.975	–

second reused samples were found to be very similar to that of the Co/AC sample suggesting that the amount of cobalt oxide leached from the sample was small and the reaction proceeded under the heterogeneous mode.

#### 4. Conclusion

AC and Co/AC exhibited phenol adsorption in aqueous solution. Co/AC also exhibited high activity for activation of PMS to produce sulphate radicals for phenol oxidative decomposition. Several factors such as phenol concentration, Co loading, catalyst loading, oxidant concentration, and temperature influenced the decom-

position rate and removal efficiency of phenol. The kinetic study showed that phenol degradation followed the first order model and activation energy was obtained to be 59.7 kJ/mol. Co/AC also showed good activity for activation of PMS in phenol oxidation after regeneration and Co leaching from Co/AC solid phase was much less, making it as a promising heterogeneous catalyst for organic oxidation with sulphate radicals.

#### Acknowledgments

We acknowledge CRC CARE, Australia, for the financial support. PRS is thankful to Dr Elaine Miller, Department of Applied Physics, Curtin University of Technology for her technical advice on SEM and EDS.

#### References

- [1] R.G. Rice, *Ozone Sci. Eng.* 18 (1997) 477–515.
- [2] E. Neyens, J. Baeyens, *J. Hazard. Mater.* 98 (2003) 33–50.
- [3] S. Chiron, A. Fernandez-Alba, A. Rodriguez, E. Garcia-Calvo, *Water Res.* 34 (2000) 366–377.
- [4] P.R. Gogate, A.B. Pandit, *Adv. Environ. Res.* 8 (2004) 501–551.
- [5] S. Malato, J. Blanco, D.C. Alarcon, M.I. Maldonado, P. Fernandez-Ibanez, W. Gernjak, *Catal. Today* 122 (2007) 137–149.
- [6] S. Wang, *Dyes Pigments* 76 (2008) 714–720.
- [7] M. Perez, F. Torrades, X. Domenech, J. Peral, *Water Res.* 36 (2002) 2703–2710.
- [8] P.R. Shukla, S. Wang, H.M. Ang, M.O. Tadé, *Sep. Purif. Technol.* 70 (2010) 338–344.
- [9] P. Shukla, I. Fatimah, S. Wang, H.M. Ang, M.O. Tadé, *Catal. Today*, doi:10.1016/j.cattod.2010.04.015.
- [10] B. Neppolian, J.S. Park, H. Choi, *Ultrason. Sonochem.* 11 (2004) 273–279.
- [11] K.H. Chan, W. Chu, *Water Res.* 43 (2009) 2513–2521.
- [12] G.P. Anipsitakis, D.D. Dionysiou, *Environ. Sci. Technol.* 37 (2003) 4790–4797.
- [13] S.K. Ling, S. Wang, Y. Peng, *J. Hazard. Mater.* 178 (2010) 385–389.
- [14] J. Fernandez, P. Maruthamuthu, A. Renken, J. Kiwi, *Appl. Catal. B: Environ.* 49 (2004) 207–215.
- [15] G.P. Anipsitakis, E. Stathatos, D.D. Dionysiou, *J. Phys. Chem. B* 109 (2005) 13052–13055.
- [16] X.Y. Chen, J.W. Chen, X.L. Qiao, D.G. Wang, X.Y. Cai, *Appl. Catal. B: Environ.* 80 (2008) 116–121.
- [17] Q. Yang, H. Choi, Y. Chen, D.D. Dionysiou, *Appl. Catal. B: Environ.* 77 (2008) 300–307.
- [18] Q. Yang, H. Choi, D.D. Dionysiou, *Appl. Catal. B: Environ.* 74 (2007) 170–178.
- [19] W. Zhang, H.L. Tay, S.S. Lim, Y. Wang, Z. Zhong, R. Xu, *Appl. Catal. B: Environ.* 95 (2010) 93–99.
- [20] P. Shukla, S. Wang, K. Singh, H.M. Ang, M.O. Tadé, *Appl. Catal. B: Environ.* 99 (2010) 163–169.
- [21] S.B. Wang, G.Q. Lu, *Carbon* 36 (1998) 283–292.